Spectroscopic properties and relaxation processes of impurity molecules in solids. II. Vibrational relaxations

Spectroscopic properties and relaxation processes of impurity molecules in solids. II. Vibrational relaxations

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We have calculated the vibrational relaxation rates for HCl (DCl)/Ar matrix systems. The quantitative agreement between our calculations and experimental data is fairly good. Our approach based on the adiabatic approximation can consistently treat the eigenvalue problems and vibrational relaxation processes for diatomic molecules embedded in monatomic crystals. The adiabatic approximation is used to separate high (intramolecular vibration) and low frequency modes (molecular rotation and lattice vibration). The nonadiabatic couplings (the kinetic energy operators for the low frequency modes) induce the vibrational relaxation processes. Our numerical calculations support the mechanism proposed by Bondybey and Brus that for small hydrides molecular rotation is the dominant accepting mode. The A_{1g} totally symmetric lattice modes in the classification by the irreducible representations of the substitutional site symmetry O_h are shown to be dominant to accept the energy mismatch between initial and final rotational levels. For the DCl/Ar system, we have found that the mixing of initial rotational levels due to the rotation-lattice vibration coupling is responsible for the vibrational relaxation. The calculated relaxation rate for DCl is smaller than that of HCl by one order of magnitude.

I. INTRODUCTION

The vibrational relaxation processes of guest diatomic molecules in solid matrices have been studied experimentally[1~3] and theoretically.[4] Many authors have examined the effects of delocalized lattice phonons, localized modes, molecular rotation, and rotation-translation coupling, etc., taking into account the interaction between a guest molecule and its surrounding neighbors. Most of the earlier theoretical studies have dealt with the simplest relaxation mechanism called the multiphonon relaxation in which the intramolecular vibrational energy of the guest is released directly into the delocalized lattice phonons. These works[5~10] have predicted that the vibrational relaxation rate depends strongly on temperature and decreases exponentially with the increase of the intramolecular vibrational frequency. It has been reported that heavy diatomics S_2,[11,12] C_2^-,[13] O_2,[14] probably relax via multiphonon processes. In contrast, small hydride molecules such as HCl,[15] OH,[16] and NH,[17] etc., do not follow the mechanism of the multiphonon relaxation: They show very weak temperature dependence in relaxation rates, and the hydrides relax faster than the corresponding deuterides. To explain these tendencies, Brus and Bondybey,[16] noticing the larger rotational constants for hydrides, assumed that the intramolecular vibrational energy is accepted principally by the rotation of guest hydride molecules. Later Legay[1] correlated existing experimental data with this assumption.

Several groups have developed models to account for the role of molecular rotations in the vibrational relaxation processes. Freed et al.[18,19] have employed a two-dimensional model in which the intramolecular vibration-rotation coupling is considered. Their model predicts that the relaxation rate decreases exponentially with the square root of (intramolecular vibrational frequency/rotational constant), and depends on temperature weakly. Diestler et al.[20] have studied the role of molecular rotations in NH, OH, and HCl molecules by adopting a model similar to that of Freed et al. Knittel and Lin[21] have extended those models by including the effect of lattice phonons explicitly. Gerber and Berkowitz[22~24] have developed a three-dimensional model. Their calculated relaxation rates of NH and ND in Ar matrix seem to be in a good agreement with the experimental results. However, in these studies, the interaction potential between a guest molecule and its surrounding host atoms has been estimated based on some assumptions, especially, the intramolecular coordinate dependence of the interaction potential. Moreover, the treatments of lattice vibration are incomplete in the sense that the presence of a guest molecule modifies the phonon structure, especially, in its neighborhood.

Another critical point is concerned with perturbations inducing the vibrational relaxation. The interaction potentials between a guest molecule and its neighbors have been treated as the perturbations in almost all theories except for a treatment proposed by Lin et al.[10] In their treatment, doorway states (initially prepared states by sources) are written as a single product of single-mode functions which are obtained from the case of the adiabatic approximation. Then the nonadiabatic couplings between high (intramolecular vibration) and low frequency modes induce the vibrational relaxation. Usually the adiabatic approximation provides good "doorway states."[25]

In a previous paper[26] (referred to as paper I), we have proposed a theory based on the adiabatic approximation for systems of a diatomic molecule embedded in a monatomic crystal. The adiabatic approximation is used to separate the numerous degrees of freedom of the system into the intramolecular vibrational degree of freedom and the other degrees of freedom (containing molecular rotation and lattice vibration). The Green's function method has been used to treat lattice vibration. We have performed the calculation of rotational spectral shifts of HCl and DCl in rare gas ma-

trices adopting the M5 potentials proposed by Hutson and Howard.[27]

In this paper, following the idea of the adiabatic approximation, we calculate the vibrational relaxation rates for HCl (DCl)/Ar systems. In Sec. II, an expression giving the vibrational relaxation rate is presented. The dominant nonadiabatic coupling inducing the vibrational relaxation is the kinetic energy operator for the molecular rotation. As in paper I, the effect of lattice vibration is taken into consideration appropriately with the aid of the Green's function method.[28] In Sec. III, we report the numerical results of the vibrational relaxation rates for HCl and DCl/Ar systems. For the numerical calculations, we introduce the dependence on the intramolecular vibrational coordinate into the M5 potentials in a tentative way; the original M5 potentials do not include the intramolecular coordinate. Finally, in Sec. V, we summarize and discuss our results.

II. THEORY

We present a theory to calculate the vibrational relaxation rate of an intramolecular mode. In paper I, we have employed the adiabatic approximation in which the intramolecular vibration of high frequency is separated from the lattice vibration and molecular rotation. The excited intramolecular vibrational states determined by the adiabatic approximation are regarded as good doorway states, since the adiabatic eigenvalues and eigenfunctions are very accurate and since only the transitions between the levels belonging to different intramolecular vibrational levels assigned by the adiabatic approximation are optically allowed in infrared region. In this paper we adopt the adiabatic basis set as doorway states and treat the vibrational relaxation as nonadiabatic processes.

In the adiabatic approximation proposed in paper I the perturbations to induce the vibrational relaxation are the nonadiabatic coupling through the kinetic energy operators of low frequency modes, i.e., molecular rotation and lattice vibration. This coupling scheme is obtained by using the same procedure as in Ref. 10. We have studied the effects of both kinetic energy operators. According to our result the nonadiabatic coupling due to the kinetic operator of molecular rotation is much larger than that of lattice vibration. Thus, we neglect the latter in the following treatment. In what follows we shall recall some results obtained in paper I, which are necessary for the calculation of the vibrational relaxation rates.

The adiabatic wave function for the nth intramolecular vibrational level is as follows:

$$|n\rangle = \left(\sqrt{\frac{\mu\Omega'}{\pi\hbar}} \Big/ 2^n \cdot n! \right)^{1/2}$$
$$\times H_n\left(\sqrt{\frac{\mu\Omega'}{\hbar}} Q' \right) \exp\left(-\frac{\mu\Omega'}{2\hbar} Q'^2 \right) , \qquad (1)$$

where Ω' and Q' are related to the interaction between a guest molecule and its surrounding host atoms, $\hat{H}_{ML}$ by

$$\Omega'^2 = \Omega^2 + \frac{1}{\mu} \left(\frac{\partial^2 \hat{H}_{ML}}{\partial Q^2} \right)_{Q=0} , \qquad (2)$$

$$Q' = Q + \frac{1}{\mu\Omega'^2} \left(\frac{\partial \hat{H}_{ML}}{\partial Q} \right)_{Q=0} . \qquad (3)$$

Q, Ω, and μ are the normal coordinate, vibrational frequency, and reduced mass of the isolated molecule, respectively. The adiabatic wave function $|n\rangle$ depends parametrically on the rotational angles, the center-of-mass of the molecule, and the host atom coordinates through $(\partial \hat{H}_{ML}/\partial Q)_{Q=0}$ and $(\partial^2 \hat{H}_{ML}/\partial Q^2)_{Q=0}$. For the HCl(DCl)/Ar systems, $\hat{H}_{ML}$ can be expressed as the sum of the interaction potentials between the HCl (DCl) and the host atoms. It will be sufficient in this case to take into account the nearest neighbor interactions alone [see Eq. (19)].

The Hamiltonian for molecular rotation and lattice vibration in the nth intramolecular vibrational state $\hat{H}_n$ is decomposed into three parts, rotational $\hat{H}_{n;r}$, lattice vibrational $\hat{H}_{n;v}$, and their coupling $\hat{H}_{n;rv}$,

$$\hat{H}_n = \hat{H}_{n;r} + \hat{H}_{n;v} + \hat{H}_{n;rv} + E^0(n) , \qquad (4)$$

where $E^0(n)$ is the energy for the nth intramolecular vibrational state. We have evaluated $\hat{H}_n$ up to the order of $1/\Omega^2$. The diagonal correction term due to the kinetic energy operators of the low frequency modes has been neglected, since its order of approximation is higher than $1/\Omega^2$. In paper I, we have shown that the HCl molecule trapped in Ar matrix rotates freely. Therefore, $\hat{H}_{n;r}$ can be chosen to be the kinetic energy operator of molecular rotation

$$\hat{H}_{n;r} = \frac{\hat{J}^2}{2I} , \qquad (5)$$

where I is the moment of inertia, and the angular momentum operator $\hat{J}^2$ is given by

$$\hat{J}^2 = -\hbar^2 \left(\frac{\partial^2}{\partial\theta^2} + \cot\theta \cdot \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right) . \qquad (6)$$

θ and ϕ are the angles for molecular rotation.

The lattice, in our theory, is composed of the center-of-mass of the molecule and the host atoms. The isotropic interaction between the guest molecule and its surrounding host atoms, which affects the phonon structure of the perfect crystal, is regarded as the potential between the center-of-mass of the molecule and the host atoms. $\hat{H}_{n;v}$ has been expanded up to the second order of the small displacements of lattice components (i.e., the harmonic approximation). In our theory, instead of solving the eigenvalue problem for $\hat{H}_{n;v}$ directly, we employ an alternative approach, i.e., the Green's function method, which turns out to be more convenient and powerful in the investigation of the lattice vibration of the solid systems with point defects.

In the HCl/Ar system, the rotation-lattice vibration coupling $\hat{H}_{n;rv}$ gives considerable shifts and widths to the rotational levels of the free rotor.[26]

A. The relaxation rate constant

In calculating the vibrational relaxation rate, the role of $\hat{H}_{n;rv}$ is secondary. The reason is as follows. The rotation-lattice vibration coupling has little effect on high rotational levels (which are supposed to be the

final rotational levels in the vibrational relaxation processes), because the energy spacings between such levels are much larger than the phonon frequencies. In contrast, for low lying rotational levels, which are supposed to be the initial rotational levels, the rotation-lattice vibration coupling gives rise to the shifts and widths. The widths of the initial levels do not have significant effects in the case of the relaxation into continua. The shifts affect the energy gap between the initial and final rotational levels. In HCl/Ar system, the energy of the $J = 0$ level is shifted by about 10 cm^{-1}, which can be included into the energy gap. However, for simplicity, we do not include these shifts in the present treatment. Moreover, there is a mixing mechanism due to the rotation-lattice vibration coupling that mixes the levels of low lying rotational levels. As will be discussed later (Sec. III), this mixing is not important for the HCl/Ar system. Hence we start with the case in which $\hat{H}_{n;rv}$ is absent. In this case, the adiabatic basis set is given by

$$\{\,|n\rangle\,|JM\rangle\,|\{v\}\rangle\,\}\ ,\tag{7}$$

where J and M are the rotational quantum numbers and $\{v\}$ denotes the lattice vibrational states. In the basis set of Eq. (7), the vibrational relaxation rate for the transition from (nJM) to $(n'J'M')$, $W(n,J,M \to n',J',M')$, is given by the Fermi golden rule

$$W(n,J,M \to n',J',M') = \frac{2\pi}{\hbar}\sum_{v}\sum_{v'}\rho_{n;vv}$$

$$\times\,|\langle\{v'\}|\langle J'M'|\langle n'|\frac{\hat{J}^2}{2I}\,|n\rangle\,|JM\rangle\,|\{v\}\rangle|^2$$

$$\times\,\delta(E_{n'J'M'\{v'\}} - E_{nJM\{v\}})\ ,\tag{8}$$

where $\rho_{n;vv}$ is the Boltzmann factor for the lattice vibration in the nth intramolecular vibrational state. $E_{nJM\{v\}}$ represents the eigenvalues of $\hat{H}_n$. Introducing the integral representation for the delta function into Eq. (8), we obtain the generating function form for the relaxation rate

$$W(n,J,M \to n',J',M') = \frac{1}{\hbar^2}\int_{-\infty}^{\infty}dt\,\mathrm{Tr}\,\hat{\rho}_n\langle JM|\langle n|\frac{\hat{J}^2}{2I}|n'\rangle$$

$$\times\exp\left[-\frac{it}{\hbar}\hat{H}_{n'}\right]|J'M'\rangle\langle J'M'|\langle n'|\frac{\hat{J}^2}{2I}|n\rangle\exp\left[\frac{it}{\hbar}\hat{H}_n\right]|JM\rangle\ ,\tag{9}$$

where $\hat{\rho}_n$ is the density matrix of the lattice vibration. Tr means the trace over the lattice vibrational degrees of freedom. Applying the Condon-like approximation, in which the matrix element $|\langle JM|\langle n|\hat{J}^2/2I|n'\rangle|J'M'\rangle|^2$ is evaluated at an equilibrium distance between the center-of-mass of the molecule and the nearest neighbor host atom j, R_{Gj}^0, we obtain

$$W(n,J,M \to n',J',M') = \frac{1}{\hbar^2}\,|C(n,J,M \to n',J',M')|^2$$

$$\times\int_{-\infty}^{\infty}dt\exp\left[\frac{it}{\hbar}\Delta E^0 + \frac{it}{\hbar}B_nJ(J+1) - \frac{it}{\hbar}B_{n'}J'(J'+1)\right]$$

$$\times\mathrm{Tr}\left[\hat{\rho}_n\exp\left(\frac{it}{\hbar}\hat{H}_{n;v}\right)\exp\left(-\frac{it}{\hbar}\hat{H}_{n';v}\right)\right],\tag{10}$$

where

$$C(n,J,M \to n',J',M') = \langle JM|\langle n|\frac{\hat{J}^2}{2I}|n'\rangle|J'M'\rangle_{R_{Gj}=R_{Gj}^0}\ ,\tag{11}$$

and the intramolecular vibrational energy gap ΔE^0 is

$$\Delta E^0 = E^0(n) - E^0(n')\ .\tag{12}$$

B_n is the rotational constant in the nth intramolecular vibrational state. If we let

$$\hat{H}_{n';v} = \hat{H}_{n;v} + \hat{V}$$

then we have

$$W(n,J,M \to n',J',M') = \frac{1}{\hbar^2}\,|C(n,J,M \to n',J',M')|^2$$

$$\times\int_{-\infty}^{\infty}dt\exp\left\{\frac{it}{\hbar}[\Delta E^0 + B_nJ(J+1) - B_{n'}(J'+1)]\right\}$$

$$\times\mathrm{Tr}\left\{\hat{\rho}_n\exp_-\left[-\frac{i}{\hbar}\int_0^t d\tau\,\hat{V}(\tau)\right]\right\}\ ,\tag{13}$$

where $\exp_-[\cdots]$ denotes the usual time ordered exponential, and

$$\hat{V}(\tau) = \exp\left(\frac{i\tau}{\hbar}\hat{H}_{n;v}\right)\hat{V}\exp\left(-\frac{i\tau}{\hbar}\hat{H}_{n;v}\right)\ .\tag{14}$$

In the case where $\hat{V}$ is a function containing only the linear terms of lattice displacements, we find

$$T_r\left\{\hat{\rho}_n\exp_-\left[-\frac{i}{\hbar}\int_0^t d\tau\,\hat{V}(\tau)\right]\right\}$$

$$= \exp\left[-\frac{1}{\hbar^2}\int_0^\tau d\tau_1\int_0^{\tau_1}d\tau_2\langle\hat{V}(\tau_1)\hat{V}(\tau_2)\rangle\right]$$

$$= \exp\left[-\frac{1}{\hbar^2}\int_0^t d\tau(t-\tau)\langle\hat{V}(\tau)\hat{V}\rangle\right]\ ,\tag{15}$$

where

$$\langle\hat{V}(\tau_1)\hat{V}(\tau_2)\rangle = T_r\,\hat{\rho}_n\,\hat{V}(\tau_1)\hat{V}(\tau_2)\ .\tag{16}$$

If nonlinear terms exist, then the cumulant expansion method can be used.[29]

B. The effect of the change of host atom equilibrium position

In this subsection we determine $\hat{V}$ for the vibrational relaxation. For this purpose we shall choose $\{R_{Gj}^0\}$ as the equilibrium distance in the nth intramolecular vibrational state. Retaining only linear terms of the small displacements $\{\Delta R_j\}$ of host atoms from their equilibrium positions $\{R_j^0\}$, we have [see Eqs. (3)–(7) in paper I]

$$\hat{V} = \frac{1}{4\pi}\,[D_1(n') - D_1(n)]\sum_j\,(\sin\theta_j^0\cos\phi_j^0\,\Delta R_{jx}$$

$$+ \sin\theta_j^0\sin\phi_j^0\,\Delta R_{jy} + \cos\theta_j^0\,\Delta R_{jz})\ ,\tag{17}$$

where

$$D_1(n') - D_1(n) = \frac{\hbar(n'-n)}{2\mu\Omega}\left[\frac{\partial}{\partial R_{Gj}}\left(\frac{\partial^2 V_0(R_{Gj},Q)}{\partial Q^2}\right)_{Q=0}\right]_{R_{Gj}=R_{Gj}^0}\ .\tag{18}$$

(θ_j^0, ϕ_j^0) represents the direction of $\{R_j^0\}$ from the center of the substitutional site. V_0 is the isotropic part of $\hat{H}_{ML}$. $\hat{H}_{ML}$ is expanded in terms of the Legendre polynomials as follows:

$$\hat{H}_{ML} = \sum_j \sum_{l=0}^{\infty} \frac{2l+1}{4\pi} V_l(R_{Gj}, Q) P_l(\cos\beta_j)$$

$$= \sum_j \sum_l \sum_{m=-l}^{l} V_l(R_{Gj}, Q) Y_{lm}^*(\theta_j, \phi_j) Y_{lm}(\theta, \phi) , \qquad (19)$$

where β_j is the angle between the molecular axis and the vector $\mathbf{R}_{Gj}$.

Carrying out the summation over j in Eq. (17), we obtain

$$\hat{V} = \gamma_{nn'} S_{A_{1g}} , \qquad (20)$$

where

$$\gamma_{nn'} = \frac{\sqrt{3}\,\hbar(n'-n)}{4\pi\mu\Omega} \left[\frac{\partial}{\partial R_{Gj}} \left(\frac{\partial^2 V_0(R_{Gj}, Q)}{\partial Q^2} \right)_{Q=0} \right]_{R_{Gj}=R_{Gj}^0} , \qquad (21)$$

and $S_{A_{1g}}$ is the symmetry coordinate belonging to the A_{1g} representation of the substitutional site symmetry O_h,

$$S_{A_{1g}} = \frac{1}{\sqrt{24}} (\Delta R_{1x} + \Delta R_{1z} + \Delta R_{2y} + \Delta R_{2z} - \Delta R_{3x} + \Delta R_{3z}$$

$$- \Delta R_{4y} + \Delta R_{4z} + \Delta R_{5x} + \Delta R_{5y} - \Delta R_{6x} - \Delta R_{7x}$$

$$- \Delta R_{7y} + \Delta R_{8x} - \Delta R_{8y} + \Delta R_{9x} - \Delta R_{9z} + \Delta R_{10y}$$

$$- \Delta R_{10z} - \Delta R_{11x} - \Delta R_{11z} - \Delta R_{12y} - \Delta R_{12z}) . \qquad (22)$$

The positions of the 12 nearest neighbor atoms numbered from 1 to 12 are listed in Appendix B of paper I. Due to the linear term $\gamma_{nn'} S_{A_{1g}}$ the equilibrium positions of host atoms change along the $S_{A_{1g}}$ coordinate, depending on the intramolecular vibrational states. The totally symmetric modes of lattice vibration are interpreted as accepting modes; needless to say, this reminds us of electronic relaxation in which the totally symmetric modes of molecules having displacements between two electronic states are accepting modes in the nonradiative relaxation of electronic energy.

The correlation function $\langle \hat{V}(\tau)\hat{V} \rangle$ involved in Eq. (15) can be evaluated by using the Green's function method.[26,28] Taking advantage of the Green's function of the A_{1g} symmetry $G_{A_{1g}}$, we have

$$\langle S_{A_{1g}}(\tau) S_{A_{1g}} \rangle = \left(-\frac{\hbar}{\pi} \right) \int_{-\infty}^{\infty} d\omega \exp(-i\omega\tau) \frac{\text{sgn}\,\omega}{1-\exp(-\beta\hbar\omega)}$$

$$\times I_m G_{A_{1g}}(\omega^2) . \qquad (23)$$

Inserting Eq. (23) into Eq. (15) yields

$$\exp\left[-\frac{\gamma_{nn'}^2}{\hbar^2} \int_0^t (t-\tau)\langle S_{A_{1g}}(\tau) S_{A_{1g}} \rangle \right] = \exp[v(t)] , \qquad (24)$$

where

$$v(t) \equiv \frac{\gamma_{nn'}^2}{\hbar^2} \left(\frac{\hbar}{\pi} \right) \int_{-\infty}^{\infty} d\omega \left[-\frac{it}{\omega} - \frac{1}{\omega^2}(\exp(-it\omega)-1) \right]$$

$$\times \frac{\text{sgn}\,\omega}{1-\exp(-\beta\hbar\omega)} I_m G_{A_{1g}}(\omega^2) . \qquad (25)$$

The Green's function $G_{A_{1g}}$ for the perturbed crystal is related to that of the perfect crystal $G_{A_{1g}}^0$,

$$G_{A_{1g}}(\omega^2) = \frac{G_{A_{1g}}^0(\omega^2)}{1 + \frac{1}{4}\Delta A G_{A_{1g}}^0(\omega^2)} , \qquad (26)$$

with

$$\Delta A = A_{xx}'(0,0) - A_{xx}(0,0) , \qquad (27)$$

where $A_{xx}(0,0)$ and $A_{xx}'(0,0)$ are the force constants for the perfect and perturbed crystals, respectively (see paper I). $G_{A_{1g}}^0$ is given by

$$G_{A_{1g}}^0(\omega^2) = g_{xx}(0,0;\omega^2) + 2g_{xx}(011,0;\omega^2) - g_{xx}(200,0;\omega^2)$$

$$- 2g_{xx}(211,0;\omega^2) + g_{xx}(002,0;\omega^2) - g_{xx}(202,0;\omega^2) , \qquad (28)$$

where $g_{\alpha\beta}(l,l';\omega^2)$'s are the Green's functions of the perfect crystal in the site representation. l's denote the positions of lattice atoms. Taking into account only the contribution from the autocorrelation of lattice displacements, we obtain

$$G_{A_{1g}}(\omega^2) \cong \frac{g_{xx}(0,0;\omega^2)}{1 + \frac{1}{4}\Delta A g_{xx}(0,0;\omega^2)} . \qquad (29)$$

This approximation is justified by the fact that the autocorrelation of lattice atom displacements is larger than the correlation between atoms belonging to different sites. However, the quantitative justification of Eq. (29) should be examined in future studies.

When $g_{xx}(0,0;\omega^2)$ which is given by Eqs. (4-25) in paper I is inserted into Eq. (29), the imaginary part of the Green's function for the continuous band modes becomes

$$I_m G_{A_{1g}}^B = \frac{-\frac{\pi}{M_H}\nu(\omega^2)}{\left\{ 1 - \frac{\Delta A}{4M_H\omega^2}[1+S(\omega^2)] \right\}^2 + \left[\frac{\pi}{M}\Delta A\nu(\omega^2) \right]^2} , \qquad (30)$$

where M_H is the mass of host atom, $\nu(\omega^2)$ denotes the density of states for the perfect crystal per unit ω^2, and

$$S(\omega^2) = P \int_0^{\infty} \frac{\omega'^2\nu(\omega'^2)}{\omega^2-\omega'^2} d\omega'^2 . \qquad (31)$$

For the case in which an A_{1g} localized mode exists we have an extra contribution to the Green's function as

$$I_m G_{A_{1g}}^L = \frac{-\frac{\pi}{M_H}[1+S(\omega_L^2)]}{\left\{ 1 - \frac{\Delta A}{M_H}\left[\frac{d}{d\omega^2}S(\omega^2) \right]_{\omega=\omega_L} \right\}} \delta(\omega^2 - \omega_L^2) , \qquad (32)$$

where ω_L is the localized mode frequency above the cutoff frequency of band modes $[\nu(\omega_L^2)=0]$ and satisfies the following equation:

$$1 - \frac{\Delta A}{4M_H\omega_L^2}[1+S(\omega_L^2)] = 0 . \qquad (33)$$

In the presence of localized mode ω_L, $A_{xx}'(0,0)$ must be larger than $A_{xx}(0,0)$ because of $1+S(\omega_L^2)>0$.

Using Eqs. (30) and (32), we obtain the vibrational relaxation rate $W(n,J,M \to n',J')$,

$$W(n,J,M \to n',J')$$

$$= \frac{1}{\hbar^2}\left[\sum_{M'}|C(n,J,M \to n',J',M')|^2 \right] P(n,J \to n',J') , \qquad (34)$$

where

$$P(n,J \to n',J') = \int_{-\infty}^{\infty} dt \exp\left\{ \frac{it}{\hbar}\Delta E(n,J;n',J') - v(t) \right\} , \qquad (35)$$

$$\Delta E(n,J;n',J') = \Delta E^0 + B_n J(J+1) - B_{n'}J'(J'+1) , \qquad (36)$$

and

$$v(t) = \frac{\gamma_{nn'}^2}{M_H \hbar} \int_{-\infty}^{\infty} d\omega \left\{ -\frac{it}{\omega} - \frac{1}{\omega^2} [\exp(-i\omega t) - 1] \right\} \frac{\text{sgn }\omega}{1 - \exp(-\beta\hbar\omega)} \frac{\nu(\omega^2)}{\left\{ 1 - \frac{\Delta A}{4M_H\omega^2} [1 + S(\omega^2)] \right\}^2 + \left[\frac{\pi}{M_H} \Delta A \nu(\omega^2) \right]^2}$$

$$+ \frac{\gamma_{nn'}^2}{M_H\hbar} \cdot \frac{[1 + S(\omega_L^2)]}{\left\{ 1 - \frac{\Delta A}{4M_H} \left[\frac{d}{d\omega^2} S(\omega^2) \right]_{\omega=\omega_L} \right\}} \left\{ \left[-\frac{it}{\omega_L} - \frac{1}{\omega_L^2} (\exp(-i\omega_L t) - 1) \right] \frac{1}{1 - \exp(-\beta\hbar\omega_L)} \right.$$

$$\left. - \left[\frac{it}{\omega_L} - \frac{1}{\omega_L^2} (\exp(i\omega_L t) - 1) \right] \frac{1}{1 - \exp(\beta\hbar\omega_L)} \right\} \bigg/ 2\omega_L . \tag{37}$$

$\Delta E(n,J;n',J')$ is the energy mismatch between the initial and final rotational levels, which is accepted by the lattice phonons. $v(t)$ can be obtained from $\nu(\omega^2)$ by numerical integration with respect to π.

Ladouceur and Diestler[30] have proposed a pseudomolecule model consisting of a guest molecule and its surrounding host atoms to treat local lattice modes. The Green's function method applied here is believed to be the best way to include the effect of lattice vibration (Ventzl and Fischer[31] have applied the Green's function method to the electronic relaxation of a diatomic molecule embedded in one-dimensional crystal).

To complete the calculation of the vibrational relaxation rate, it is necessary to show how to evaluate $C(n,J,M \to n',J',M')$. We summarize it in the Appendix.

III. NUMERICAL RESULTS

In this section we report the results of numerical calculation of vibrational relaxation rates of HCl(DCl)/Ar systems at $T = 0$ K. $\nu(\omega^2)$ for Ar crystal is taken from Ref. 36 in paper I. In paper I, we have used the M5 potentials proposed by Huston and Howard[27] as the rare-gas HCl potentials. The M5 potential for HCl·Ar seems to be reliable in calculating the rotational levels of HCl/Ar system. However, since their potentials do not include the intramolecular vibrational coordinate (Q), they are insufficient to carry out the calculations for vibrational relaxation rates in our formulation. To include the Q dependence, we modify their potentials as follows.

The M5 potentials have a function $R_m(\beta)$, which is the distance between the center-of-mass of the molecule and the position of the potential minimum when the angle between the molecular axis and the vector from the center-of-mass of the molecule to the rare gas atom has the value β. $\beta = 0°$ corresponds to the linear configuration rare gas atom·HCl. In order to include the Q dependence we replace $R_m(\beta)$ with $R_m(Q, \beta)$ given by

$$R_m(Q, \beta) = R_m(\beta) + \left[\frac{M_H}{M_H + M_{Cl}} g_1(\beta) + \frac{M_{Cl}}{M_H + M_{Cl}} g_2(\beta) \right] Q , \tag{38}$$

where

$$g_1(\beta) = 0 \quad \text{for} \quad 0° < \beta < 90°$$
$$= \cos^2\beta \quad \text{for} \quad 90° < \beta < 180° , \tag{39}$$

and

$$g_2(\beta) = \cos^2\beta \quad \text{for} \quad 0° < \beta < 90°$$
$$= 0 \quad \text{for} \quad 90° < \beta < 180° . \tag{40}$$

This model explains the following two features which have been reported for HF/Ar by Detrich and Conn.[32] (i) The position of the potential minimum shifts toward larger values as Q increases. (ii) The Q dependence at $\beta = 90°$ is negligible. However, this model cannot explain the following feature which also has been reported by Detrich and Conn. (iii) The potential miminum becomes slightly deeper as Q increases.

We use Eq. (38) for evaluating the derivatives of V_I's with respect to Q. An important point to be noted here is that one can use the formalism developed in this paper and the previous one for determining the derivatives of V_I's with respect to Q from the measurement of spectroscopic properties and relaxation rates of impurity molecules in solids. In what follows we report the numerical results for the vibrational relaxation rate of the HCl/Ar system from the first excited intramolecular vibrational state $n = 1$.

The lattice vibrational part $P(1, J \to 0, J')$ is shown in Fig. 1 as a function of the energy mismatch $\Delta E(1,J; 0,J')$. The integration with respect to t in Eq. (35) has been done by the saddle point method. The calculated value of
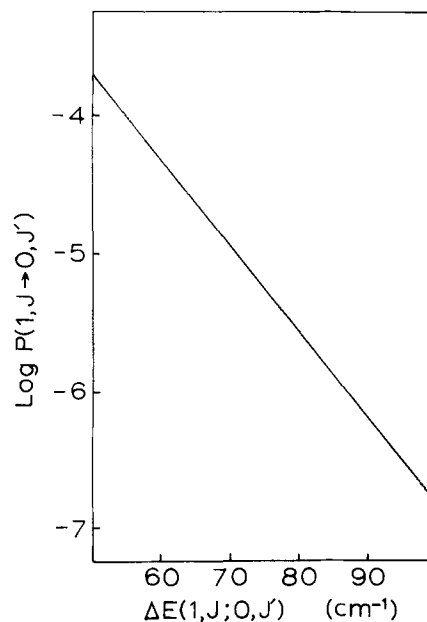

FIG. 1. The lattice vibrational part $P(1, J \to 0, J')$ as a function of the energy mismatch $\Delta E(1,J;0,J')$. The units of $P(1,J \to 0,J')$ are $1/\text{cm}^{-1}$.

$$\left[\frac{\partial}{\partial R_{Gj}}\left(\frac{\partial^2 V_0(R_{Gj},Q)}{\partial Q^2}\right)_{Q=0}\right]_{R_{Gj}=R_{Gj}^0}$$

in γ_{10} is -1.33×10^4 cm^{-1}/Å^3. We have used 3.85 Å as R_{Gj}^0.[26] In our numerical calculations, there is no localized A_{1g} mode. $P(1, J\to0, J')$ decreases very rapidly as $\Delta E(1, J; 0, J')$ increases. This means that the lattice vibration cannot accept much energy of the initial state. In contrast to this tendency, according to our calculations, the change of $\sum_{M'}|C(1, J, M\to0, J', M')|^2$ is relatively small when J' changes. Thus the dominant transition is the one to the rotational level J' whose energy is the nearest to that of the initial state, i.e., the transition whose energy mismatch is the smallest. The probabilities of the other transitions are smaller than that of the dominant one by several orders of magnitude. As a result, our calculations support the assumption[1,16] that molecular rotation is the principal accepting mode for small hydrides. In the case of the transition from $J=0$, the transition to $J'=16$ is dominant. In this case, the mismatch energy $\Delta E(1, 0; 0, 16)$ is determined to be 71 cm^{-1} from the vibrational energy gap ΔE^0 and the rotational energy of $J=16$ level, $E(J=16)$; the vibrational energy gap ΔE^0 is 2871 cm^{-1} in Ar matrix.[15,33] The rotational energy $E(J=16)$ is 2800 cm^{-1}, which includes the effect of centrifugal force.[34] It follows that $P(1, 0\to0, 16)$ is 0.11×10^{-4}/cm^{-1}. On the other hand, the calculation of $C(1, 0, 0\to0, 16, M')$ yields

$$W(1, 0, 0\to0, 16) = 3.26\times10^9\times\left[\frac{\partial V_{16}(R_{Gj}^0, Q)}{\partial Q}\right]_{Q=0}^2$$
$$\times P(1, 0\to0, 16)\,[\text{s}^{-1}]\,. \tag{41}$$

Since we have evaluated the quantity $[\partial V_{16}(R_{Gj}^0, Q)/\partial Q]_{Q=0}$ to be 0.23 cm^{-1}/Å, $W(1, 0, 0\to0, 16)$ is 1.9×10^3/s. Wiesenfeld and Moore[15] have reported that for dilute sample at 9 K the observed vibrational relaxation rate of HCl ($n=1$) is 8×10^2 s^{-1}. The agreement between our calculation and the experimental result is fairly good.

Next we shall briefly report the result for DCl/Ar system. In the Condon-like approximation, only the transitions between the rotational levels of the same parity, i.e., between even J and J' or between odd J and J', are allowed. Hence, the transition from $J=0$ to $J'=19$, of which energy mismatch is the smallest in DCl case, is not allowed. However, the rotation-lattice vibration coupling can mix the levels of $J=0$ and $J=1$. Then the wave function of the lowest rotational level is written as a linear combination of those of $J=0$ and $J=1$ (for the case of allowed transitions such as HCl/Ar system this mixing mechanism is not important). Consequently the lowest rotational level in $n=1$ can be coupled to $J'=19$ (for high rotational levels, the rotation-lattice vibration coupling is negligible). For the DCl/Ar system, including this mixing of the wave functions due to the rotation-lattice vibration coupling, we calculated the vibrational relaxation rate from the lowest rotational level of $n=1$. The relaxation rate we obtained is 1.6×10^2 s^{-1}, which is smaller than the relaxation rate of HCl by one order of magnitude. This is due to the fact that $\partial V_{18}/\partial Q$ and $\partial V_{20}/\partial Q$ appearing in the relaxation rate expression for DCl are smaller than $\partial V_{16}/\partial Q$, and the square of the coefficient of $J=1$ in the

lowest rotational level is about 0.1. Wiesenfeld and Moore[15] have reported that HCl relaxes 32 times faster than DCl for the relaxation from $n=2$ to $n=1$. Diestler and Ladouceur[35] have employed the intramolecular vibration-rotation coupling as a perturbation inducing the vibrational relaxation. In their treatment, the rotation-lattice vibration coupling gives dampings to the rotational levels. It should be noted that in our theory these two couplings have already been included in the adiabatic Hamiltonians giving the eigenfunctions and eigenvalues of the doorway states.

IV. SUMMARY AND DISCUSSION

In paper I and this paper, we have presented an approach based on the adiabatic approximation that can consistently treat the eigenvalue problems and vibrational relaxation processes for diatomic molecules embedded in monatomic crystals. In this paper we have calculated the vibrational relaxation rates for HCl(DCl)/Ar systems. Our numerical calculations agree with the experimental result fairly well, though there are limitations to the interaction potentials, and support the mechanism proposed by Bondybey and Brus[18] that the molecular rotation is the dominant accepting mode in the vibrational relaxations of small hydrides.

The energy mismatch between initial and final rotational levels is released into lattice phonons. In our calculations, the A_{1g} totally symmetric modes in the classification by the O_h substitutional site symmetry have been shown to be dominant to accept the energy mismatch. The displacement of the A_{1g} modes between the equilibrium positions of different intramolecular vibrational states results in the multiphonon relaxation of the energy mismatch as in the case of nonradiative relaxation of electronic energy. According to our calculations for HCl(DCl)/Ar systems, there is no localized A_{1g} mode.

For the DCl/Ar system, we have proposed a mechanism in which by the mixing of initial rotational levels due to the rotation-lattice vibration coupling the lowest rotational state in $n=1$ is transferred to the final rotational state of $J'=10$ in $n=0$. The calculated relaxation rate for DCl is smaller than that of HCl by one order of magnitude, which seems to be reasonable in comparison with experimental data.[1,15]

Our calculations rest on the following three points.

(i) The intramolecular coordinate dependence is tentatively introduced into the M5 potentials; (ii) the Condon-like approximation is applied to the evaluation of the matrix elements $C(n, J, M\to n', J', M')$'s; (iii) roles of the modes except the A_{1g} modes are neglected. These points will be examined in future studies.

The intramolecular coordinate dependence of the intermolecular potential functions is difficult to determine; this can be accomplished by applying our formalism to analyze the experimental results of spectroscopic properties and relaxation processes of impurity molecules in solids.

Finally we shall comment on a future study. Usually the vibrational relaxation rates of molecules take different values in different host matrices. It has been reported that the vibrational relaxation rates of small hydride increase with increasing mass of the rare gas host atoms, while for molecules controlled by multiphonon processes such as O_2 the relaxations are least efficient in Xe matrix.[3] To clear the difference between these two trends will give us better understanding in the vibrational relaxation processes.

ACKNOWLEDGMENTS

APPENDIX: EVALUATION OF THE NONADIABATIC COUPLING ELEMENT $C(n, J, M \to n', J', M')$

The nonadiabatic couplings relevant to the intramolecular vibrational wave functions are expressed as

$$\langle n' | \frac{\hat{J}^2}{2I} | n \rangle = -\frac{\hbar^2}{2I} \left[\langle n' | \frac{\partial^2}{\partial \theta^2} | n \rangle + 2 \langle n' | \frac{\partial}{\partial \theta} | n \rangle \frac{\partial}{\partial \theta} \right.$$

$$+ \cot \theta \langle n' | \frac{\partial}{\partial \theta} | n \rangle + \frac{1}{\sin^2 \theta} \langle n' | \frac{\partial^2}{\partial \phi^2} | n \rangle$$

$$\left. + \frac{2}{\sin^2 \theta} \langle n' | \frac{\partial}{\partial \phi} | n \rangle \frac{\partial}{\partial \phi} \right] . \quad \text{(A1)}$$

Using the intramolecular vibrational wave function given by Eq. (1), we obtain, for $n' = n - 1$,

$$\langle n' | \frac{\partial}{\partial \theta} | n \rangle = \sqrt{\frac{n \Omega' \mu}{2\hbar}} \left(\frac{\partial Q'}{\partial \theta} \right) , \quad \text{(A2)}$$

$$\langle n' | \frac{\partial^2}{\partial \theta^2} | n \rangle = -\frac{(n-1)}{2} \sqrt{\frac{n\mu}{2\hbar\Omega'}} \left(\frac{\partial \Omega'}{\partial \theta} \right) \left(\frac{\partial Q'}{\partial \theta} \right)$$

$$+ \sqrt{\frac{n \Omega' \mu}{2\hbar}} \left(\frac{\partial^2 Q'}{\partial \theta^2} \right) . \quad \text{(A3)}$$

The derivatives with respect to ϕ can be obtained by replacing θ's in the above equations by ϕ. By using Eqs. (2), (3), and (19) we can obtain the derivatives of Q' and Ω' with respect to θ and ϕ, which are as follows:

$$\frac{\partial Q'}{\partial \theta} = \frac{1}{2\mu\Omega'^2} \sum_{l,m}^{l \neq 0} y_{lm} [\frac{1}{2} \sqrt{(l-m)(l+m+1)} Y_{lm+1}(\theta, \phi) e^{-i\phi}$$

$$- \frac{1}{2} \sqrt{(l+m)(l-m+1)} Y_{lm-1}(\theta, \phi) e^{i\phi}] , \quad \text{(A4)}$$

$$\frac{\partial^2 Q'}{\partial \theta^2} = \frac{1}{4\mu\Omega'^2} \sum_{l,m}^{l \neq 0} y_{lm} [\sqrt{(l-m)(l+m+1)(l-m-1)(l+m+2)}$$

$$\times Y_{lm+2}(\theta, \phi) e^{-2i\phi} - 2(l^2 - m^2 + l) Y_{lm}(\theta, \phi)$$

$$+ \sqrt{(l+m)(l-m+1)(l+m-1)(l-m+2)} Y_{lm-2} e^{2i\phi}] , \quad \text{(A5)}$$

$$\frac{\partial Q'}{\partial \phi} = \frac{1}{\mu\Omega'^2} \sum_{l,m}^{l \neq 0} y_{lm} im Y_{lm}(\theta, \phi) , \quad \text{(A6)}$$

$$\frac{\partial^2 Q'}{\partial \phi^2} = -\frac{1}{\mu\Omega'^2} \sum_{l,m}^{l \neq 0} y_{lm} m^2 Y_{lm}(\theta, \phi) , \quad \text{(A7)}$$

etc., where

$$y_{lm} = \sum_j \left[\frac{\partial V_j(R_{Gj}, Q)}{\partial Q} \right]_{Q=0} Y_{lm}^*(\theta_j, \phi_j) . \quad \text{(A8)}$$

In our calculations, Ω' is replaced by Ω, and the Condon-like approximation is employed, in which R_{Gj}, θ_j, and ϕ_j in Y_{lm} are replaced by the values at equilibrium, i.e., R_{Gj}^0, θ_j^0, and ϕ_j^0.

In order to calculate $C(n, J, M \to n', J', M')$, we have to perform the integrations over the rotational angles θ and ϕ. We have carried out the integrations by using

$$Y_{lm}(\theta, \phi) = (-1)^m \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l-m)!}} P_l^m(\cos \theta) e^{im\phi} , \quad \text{(A9)}$$

where the associated Legendre polynomials P_l^m's can be expressed as, for positive m

$$P_l^m(\cos \theta) = (-1)^{l+m} \frac{(\sin \theta)^m}{2^m} \sum_{r=0}^{l-m} (-1)^r$$

$$\times \frac{(l+m+r)!}{r!(m+r)!(l-m-r)!} \cos^{2r} \frac{\theta}{2} . \quad \text{(A10)}$$

When m is negative, the following relation is available:

$$P_l^{-|m|} = (-1)^{|m|} [(l - |m|)! / (l + |m|)!] P_l^{|m|} . \quad \text{(A11)}$$

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